

# MEASUREMENTS OF INTERFACE SUPERCOOLING WITH THE OPTICAL PYROMETER IN CRYSTAL GROWTH FROM THE MELT<sup>1</sup>

S.V.Bykova<sup>2</sup>, V.S.Dozhdikov<sup>3</sup>, V.D.Golyshev<sup>2,4</sup>, M.A.Gonik<sup>2</sup>, V.A.Petrov<sup>2</sup>,  
V.N.Senchenko<sup>2</sup>, V.B.Tsvetovsky<sup>2</sup>.

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<sup>2</sup>Center for Thermophysical Researches “Thermo”, Institutskaia Str. 1, 601650, Alexandrov, Russia.

<sup>3</sup>Institute for High Energy Density, AIHT RAS, Moscow, Russia.

<sup>4</sup> Corresponding author: [thermo.ltd@relcom.ru](mailto:thermo.ltd@relcom.ru)

## ABSTRACT

Construction and parameters of an optical high-resolution pyrometer, designed for interface supercooling  $\Delta T$  measurement, are described. Supercooling is determined by measuring of interface brightness temperature  $T_b$  through the growing semitransparent crystal. The results of *in situ* supercooling measurement at  $\text{Bi}_3\text{Ge}_4\text{O}_{12}$  crystal growth from melt, obtained with the use of a pyrometer, are discussed. The influence of thermal conditions on the inaccuracy of interface supercooling measurement is studied. In case of influence of thermal conditions the method of correction of experimental data is analyzed.

KEY WORDS: brightness temperature; crystals; optical pyrometer; melts; supercooling.

## 1. INTRODUCTION

To determine dependence  $V/\Delta T$  of crystal growth rate  $V$  on the value of interface supercooling  $\Delta T$  is of great importance for finding out the mechanisms of interfacial kinetics and for improving the quality of the grown crystals [1]. In ref. [2] a new technique of *in situ*  $\Delta T$  measurement was proposed. It is based on interface brightness temperature  $T_b$  measurement. It is done with the use of an optical pyrometer, which is being focused through the growing crystal on the interface surface.  $\Delta T$  can be found by the equation:  $\Delta T = T_b^m - T_b^v$ , where  $T_b^m$  is interface brightness temperature, measured in absence of the growth,  $T_b^v$  – is brightness temperature at growth rate  $V$ .  $T_b^m$  corresponds to the melting point,  $T_b^v$  corresponds to the supercooled interface temperature at growth rate  $V$ . Earlier these measurements were carried out with the use of a high-accuracy laboratory optical pyrometer with a disappearing thread LOP-72. Its target size is 8 mm in diameter.

In view of the fact that the value of supercooling depends upon the coordinates on the interface, measurement by the instrument with such a large diameter of the target results in averaging of the data. This averaging causes considerable errors when maximum interface supercooling is being determined, as the result has to be restored from the thermal conditions and interface morphology [6,7]. The method of measurement  $\Delta T$ , proposed in ref. [2] is based on the supposition of crystal transparency. This supposition is fair for high-quality crystals and it considerably limits the possibility of obtaining

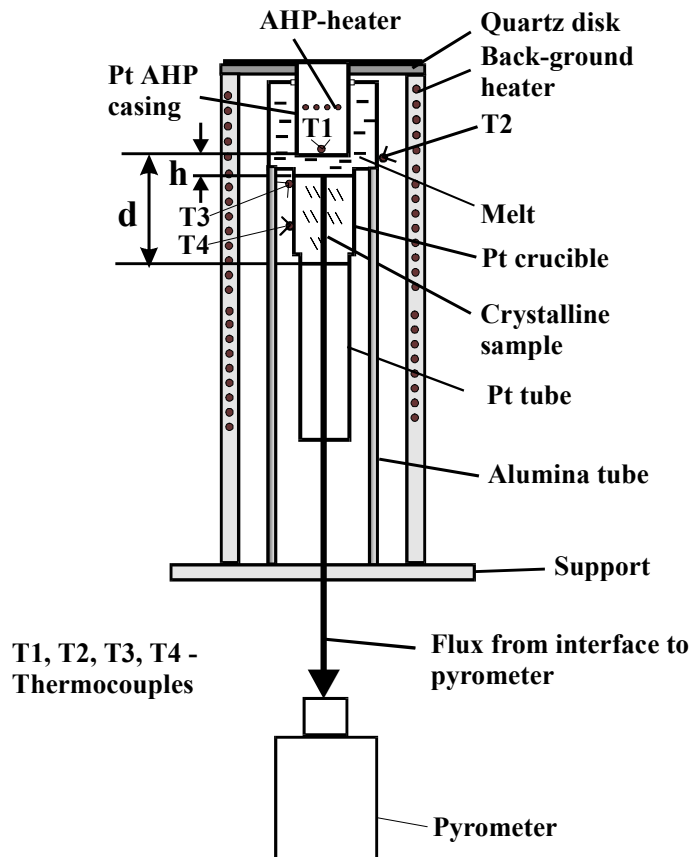
data in general. Hence there arises a task to determine the conditions of using the new method in cases when the crystal absorption coefficient is nonzero.

The present work describes the schematics of the specialized high-sensitive computerized optical pyrometer with a target spot of 1.2 mm in diameter, developed for supercooling measurement. The results, obtained with the use of the pyrometer are presented. The possibility of applying the method of supercooling measurement in case of relatively large values of the absorption coefficient, when the conditions of measurement influence  $T_b$ , is discussed.

## 2. EXPERIMENTAL SETUP AND RESERCH METHODS

### 2.1. The experimental setup and the procedure of an interface temperature measurement

The schematics of the experimental setup is shown in fig.1. A heating section provides heating of the sample up to 1100-1150° C in an air. The device is located on a support, under which the pyrometer is fixed. Heating is done by means of a four-compartment resistance heater (further- the background heater). The sample under study of 36 mm long is placed in the lower part of the platinum AHP crucible. The upper part of the crucible is 50 mm in diameter. The lower part is 25 mm in diameter. The crucible is fixed on the additional alundum tube, which is movable.



**Fig. 1.** Schematic of experimental setups for measurement of interface supercooling.

The upper part of the crucible contains the AHP heater. It consists of a platinum casing and the platinum heating element. There is a thermocouple  $T_1$  under the heating element, its junction is welded to the bottom of the AHP heater casing. The AHP heater casing is fixed in the furnace. In the upper part of the crucible between the AHP heater casing and the sides of the crucible the powder of the studied substance is placed. Its mass was such that after its melting AHP heater would be plunged into the melt.

A temperature distribution on the AHP crucible and on the AHP heater was measured with platinum thermocouples  $T_1$ –  $T_4$ . It was maintained with a digital multi-circuit PID controller. The main microprocessor system was made on the base of the controller “Elektronika MC 1212”, the module apparatus CAMAC and digital measuring devices. Accumulation and graphic presentation of information was held by means of Data Acquisition / Switch Unit 34970A of Agilent Co. using the programme Bench Link, supplied together with this device.

The experiment was held as described below. According to the signals of the thermocouples  $T_3$ –  $T_4$  the necessary axial temperature gradient on the sample was set. The optical pyrometer was focused at the bottom of the AHP heater. Then the temperature of the furnace was increased to such a value, that a melt was appeared under the AHP heater. The given thickness of the melt layer  $h$  ( $h=2-5$  mm) was set by maintaining the necessary value of the temperature  $T_1$ . To determine the value of  $h$  one-dimensional radiative-conductive heat transfer model was used [5]. After obtaining the value of  $h$  the crystallization of the melt began. It was carried out by decreasing the temperature  $T_1$  at the necessary rate  $\alpha$ , and dependence  $T_b(t)$  was measured. When the crystallization was over the sample was exposed to melting again until the previous value  $h$  was reached, and then process of crystallization was repeated at a new rate  $\alpha$ , and a new dependence of  $T_b(t)$  was obtained. The procedure was held for three values of  $\alpha$ .

## 2.2. High-resolution pyrometer

Supercooling is determined as a difference of the brightness temperature values  $\Delta T = T_b^m - T_b^v$ . As  $T_b$  was changed unconsiderably with changing of growth rate it was necessary to make a special high-resolution pyrometer. The instrument is designed to measure two brightness and colors temperatures. The table 1 contains the main features of the pyrometer.

The objective of the pyrometer focuses the radiation of interface between a growing crystal and melt on the mirror field stop. The stop is a metallic mirror with a circular hole of 0.5 mm in diameter, set at angle of  $45^\circ$  to the optical axis of the instrument. Radiation after passing through the stop goes to the monochromator, which has a holographic diffraction grating. The spectral band of the channels at 0,795 and 0,995 nm were 30 and 40 nm correspondingly. To suppress high-order spectrums the cut-off filter on the wave length of 750 nm was used. The system of lenses of a monochromator focuses monochromatic radiation on low-noise silicon photo diodes.

Photodiodes are placed in a compact positive thermostat, which provides maintenance of constant temperature  $45^\circ\text{C}$  with  $0.02^\circ\text{C}$  accuracy and is controlled by the

microprocessor system. The signal current of photodiodes is transformed into voltage by low-noise transimpedance amplifiers. Photocurrent can change from 50 to 10000 nA in the temperature range 600-1200 °C. To provide the necessary ratio of signal/noise, the transimpedance amplifier with switched gain was developed. It was controlled by internal microprocessor.

**Table 1.** Technical features of the pyrometer.

Temperature range,	°C	600 - 1200
Resolution,	°C	0.01-0.05
Operating wavelength	$\lambda_1$ , nm	795
	$\lambda_2$ , nm	995
Spectral transmission band	$\Delta\lambda$ , nm	30/40
Instrumental error of brightness temperature measurement,	%	$\pm 0.15$
Operating distance,	L, mm	400 -450
Target size,	$\varnothing$ mm	1.2
Time of measurement,	ms	20 - 1000
Interface		RS232
Data transfer rate, baud		9600 - 115200
Weight, kg		4.8
Dimensions, mm		270×150×240

Output voltage measurement was carried out with high-stability 24-bit delta-sigma ADC with serial output interface, which had optogalvanic isolation from the microprocessor system. In dependence on the output code of ADC, the microprocessor could optimize the gain of the amplifiers. Microprocessor system ensures the recording of the primary data, calculation of two values of brightness temperatures and its sending to the computer through the interface of RS 232 type. To control the pyrometer behavior a special Windows program was developed.

Two models of absolutely black body were used for calibration of the pyrometer. Calibration constants were determined by the least squares technique using the 12 measured points in the range of 600-1200 °C. Long-term stability of the device indications was checked under control by measuring the temperature of stable black body during 8 hours.

### 2.3. The method of correction of the measured brightness temperature, taking into account the influence of optical properties of the crystal and the experiment conditions

The experimental study of an influence of thermal conditions on determination of the value  $\Delta T$  was carried out by two ways. In both cases the pyrometer was sighted on the bottom of the platinum casing of the AHP heater at room temperature. In the first case the sample was not melted and the influence of temperature gradient ( $gradT$ ) on the value  $T_b$  was studied. The signals of thermocouples on the side surface of the sample  $T_3$  and  $T_4$  (fig.1) were used to determine the value  $gradT$ . During this experiment the temperature of the AHP heater  $T_l$  (fig.1) was kept constant. Thus, if there is no

influence of the sample's own radiation and absorption, then the experiment would not exhibit the dependence of  $T_b$  on the temperature gradient. In the second case changing of  $T_b$  during melting was studied. When the sample melts, the temperature of interfacial surface does not change. So changing of  $T_b$  can be caused by the influence of measurement conditions.

Experimental data on  $T_b$  was compared with calculated data. The brightness temperature was found using the Wien formula:

$$T_b = \frac{c_2 T}{c_2 - T \lambda_0 \ln \varepsilon_{\lambda_0}}, \quad (1)$$

where  $T$  is the interfacial temperature,  $c_2 = \frac{h_p c_0}{k_B}$ ,  $k_B$  is the Boltzmann constant,  $h_p$  is the Planck's constant,  $c_0$  is the vacuum velocity of light,  $\varepsilon_{\lambda_0}$  is the effective emittance of the sample at pyrometer wavelength  $\lambda_0$ .

The value  $\varepsilon_{\lambda}$  was determined by the expresction:

$$\varepsilon = \frac{I_{rez}}{e_{b\lambda}(T_i)},$$

where  $I_{rez}$  is spectral intensity of thermal radiation, emitted by a nonisothermal sample,  $e_{b\lambda}(T_i)$  is the radiation intensity of the black body at the temperature of the melt-crystal interface, it is calculated using Planck's formula. The value  $I_{rez}$  was obtained as described in [6] on the base of numerical calculation according to a one-dimensional model.

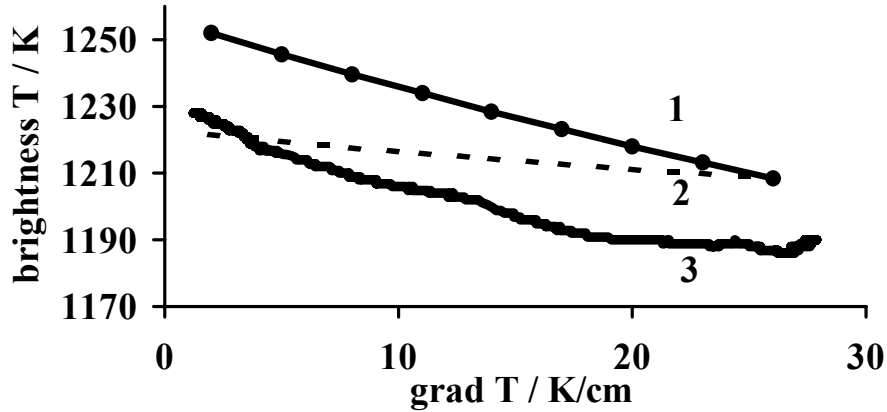
### 3. RESULTS AND DISCUSSION

#### 3.1 Features of brightness temperature behavior

On Fig.2 shows the comparison of dependence  $T_b$  (grad T) for  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) single crystal, obtained through experiment, and the results of calculation obtained with the use of the formula (1) is shown. The value grad T was found from the exprescion:  $\text{grad}T = (T_4 - T_3)/l$ , where  $l$  is the distance between the thermocouples  $T_4$  and  $T_3$  (fig.1). During the experiment the temperature in the position  $T_1$  (fig.1) was kept equal to  $1040^\circ\text{C}$ . The measurements were carried out of the wavelength of  $0.86 \mu\text{m}$ .

As one can see in Fig.2, the temperature measured with the pyrometer depends on temperature gradient. Increase of temperature gradient from 1 to 30 K/cm led to

decrease of the brightness temperature by 40 K. The decrease of  $T_b$  can be explained by the fact that the increase of temperature gradient brings to the decrease of the mean temperature of the sample. It leads to the decrease of the intensity of the sample's own thermal radiation. In its turn it leads to decrease of the  $T_b$  value.

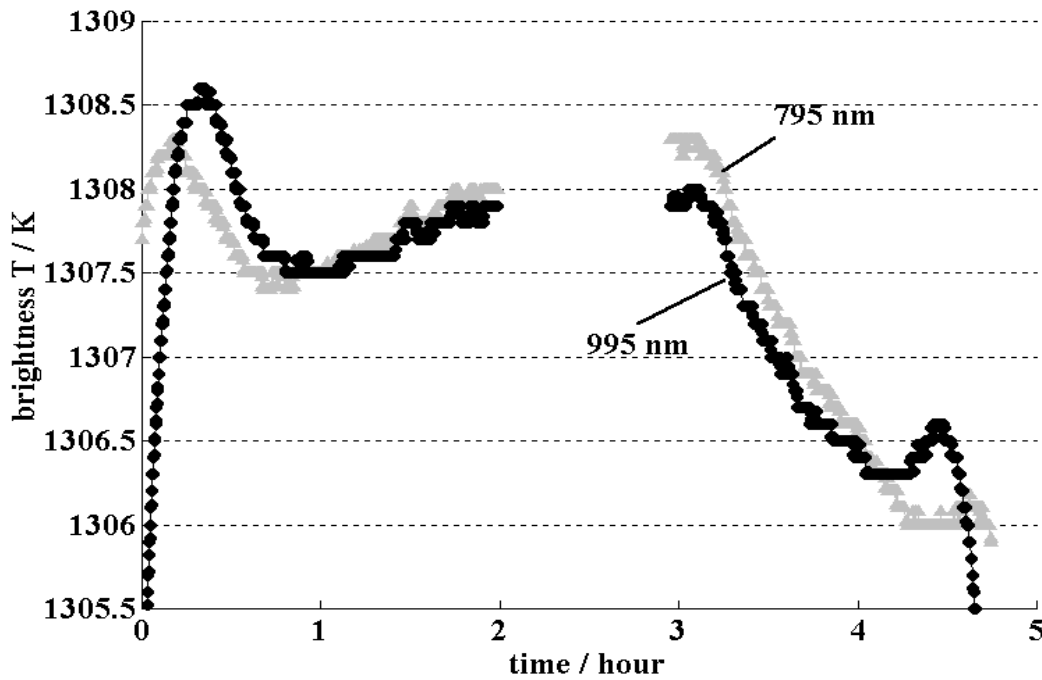


**Fig. 2.** The dependence of the brightness temperature  $T_b$  on temperature gradient of side surface of BGO sample with length 36 mm: calculation - 1 ( $\alpha = 0.3 \text{ cm}^{-1}$ ,  $\lambda = 0.86 \text{ мкм}$ ) и 2 ( $\alpha = 0.03 \text{ cm}^{-1}$ ,  $\lambda = 0.86 \text{ мкм}$ ), experiment - 3 ( $\lambda = 0.86 \text{ мкм}$ ).

Thus, the experiment demonstrates that the sample's own radiation influences the pyrometer signal. The experiment shows nonlinear dependence of  $T_b$  ( $\text{grad}T$ ). At the same time the value  $T_b$  remains practically constant in the range  $20 \text{ K/cm} < \text{grad}T < 30 \text{ K/cm}$ . Calculation with the use of the formula (1) for the different absorption coefficients (curves 1 and 2 in fig.2) draws practically linear dependence of brightness temperature on temperature gradient for the choosen parameters. Calculations were held for the emissivity of radiating surface  $\epsilon = 0.5$ . During the calculation temperature distribution in the sample was supposed to be linear.

The difference between experimental and calculated data may be explained by the two-dimensional temperature field in the sample. Temperature distribution along the sample axis is nonlinear and quite different from that on the side surface. One may suppose that starting from some value of temperature in the position  $T_4$  (Fig. 1) the influence of two-dimensionality of temperature on temperature distribution along the sample axis becomes weaker because the influence of thermal radiation on heat transfer is much more considerable than the role of the thermal conductivity.

Fig. 3 demonstrates a typical change of the pyrometer signal with time during melting (0-3 hours) and crystallization (3-4.7 hours) of the BGO sample. Visual observations showed that melting began at the pyrometer signal  $T_b \approx 1307 \text{ K}$  ( $T_l \approx 1063^\circ \text{C}$ ). Melting began with an appearance of single separate bright spots along AHP heater surface. At  $T_b \approx 1308 \text{ K}$  melting completely finished along AHP heater surface ( $t = 0.5 \text{ hour}$ ). The



**Fig. 3.** The dependence of brightness temperature on time during heating and cooling of the sample for the wave length 795 nm and 995 nm

further melting of the crystal (decreasing of length of the crystal) led to reducing of the signal at first ( $0.5 < t < 1$  hour) and then to its increase ( $1 < t < 2$  hours). Growth of the crystal at cooling of 30K/hour rate ( $3 < t < 4.7$  hours) led to decrease of the value  $T_b$  up to  $t = 4.2$  h. Then  $T_b$  increases by 0.3 K for  $\lambda = 0.995 \mu\text{m}$  and by 0.2 K for  $\lambda = 0.795 \mu\text{m}$ . After that  $T_b$  decreases again quicker than during crystallization. As visual observations showed, local extremums of the brightness temperature agree with the start of crystal melting ( $0.5 < t < 1$  hour) and the finish of melt crystallization ( $4 < t < 4.5$  hours). At present the nature of such  $T_b$  behavior is not evident.

Fig. 3 shows that during melting (length decreasing) of the sample ( $1 < t < 2$  hours) the brightness temperature increases approximately by 0.5 K. It confirms the fact that the experiment conditions influence on the results of measurements. The influence of the sample on the brightness temperature, measured with the pyrometer, depends on the length, temperature distribution and optical properties of the sample [6]. Calculations and experimental verification according to the marks, left by crystallization front after cooling and cutting the sample( see [5]) showed that the value  $h$  before crystallization reached 5-6 mm. Thus, melting of the sample gave the change of its length from 36 mm at the beginning of melting to 30 mm at the end. Calculations according to the formula

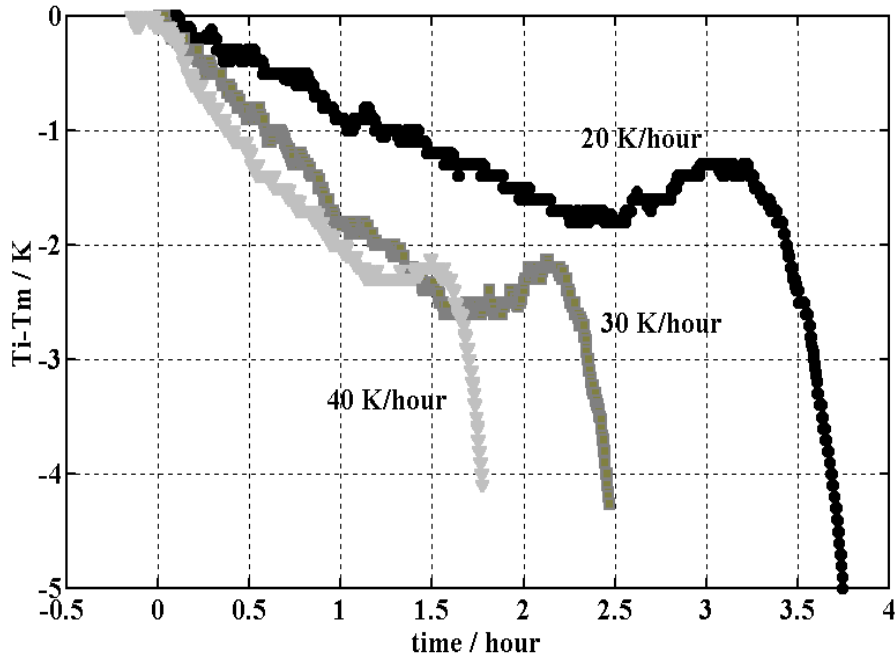
(1) were carried out for  $\alpha=0.03 \text{ cm}^{-1}$  and linear temperature distribution in the sample, which was determined by the value  $\text{grad}T=(T_4-T_3)/l$  on the side surface of the crystal. The result of calculation showed that the change of the length brings to increase of the brightness temperature by 0.5 K, which is close to the experimental data.

### 3.2 Supercooling

The goal of the study is to find dependence of growth rate on interfacial supercooling. To achieve it the time dependence  $T_b(t)$  for different rates of melt cooling  $\alpha$  is measured. Fig. 4 shows time dependence  $\Delta T(t)$ , obtained for different rates of decreasing of AHP heater temperature  $T_l$  (Fig.1). The value  $\Delta T$  was calculated by the expression:

$$\Delta T(t)=T_b^m-T_b^i(t), \quad (2)$$

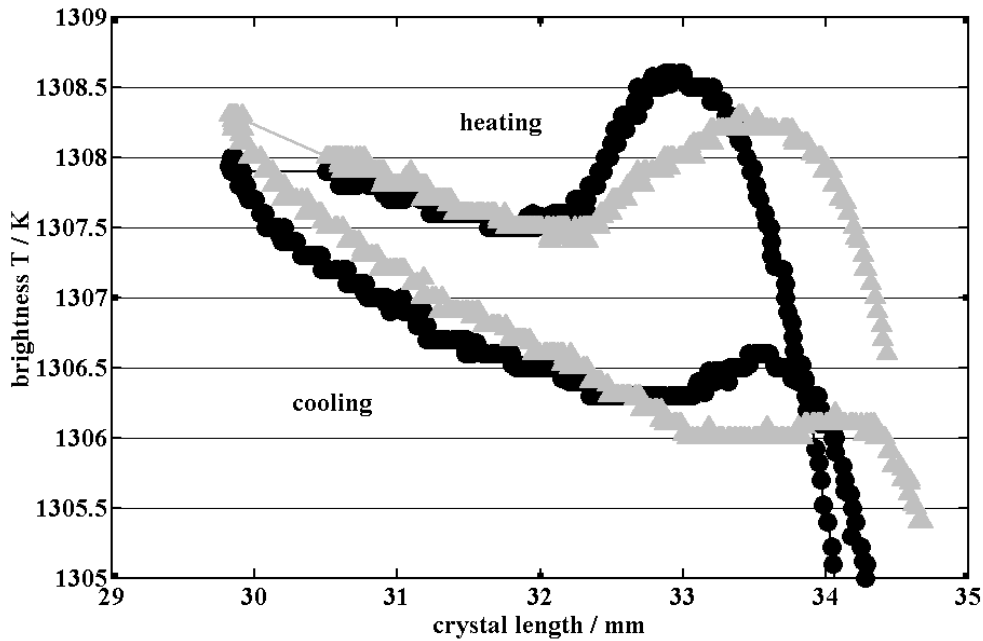
where  $t$  is time. One can see that local extremum, corresponding to the end of crystallization, appears the earlier, the higher is the cooling rate. It is connected with the fact that the more is the cooling rate, the more is the growth rate and the quicker one and the same melt layer is being crystallized.



**Fig. 4.** The time dependence of the supercooling for different cooling rate: the point of origin corresponds to start of cooling for each cooling rate.

Crystallization for cooling rate  $a = 40\text{K/h}$  started after  $t=1.2$  hours after cooling began. At the cooling rate of  $a = 40\text{K/h}$  after  $t=1.2$  hours interfacial supercooling was  $\Delta T=2.3$  K. For  $a=30\text{K/h}$  it was  $\Delta T=1.9$  K, for  $a=20\text{K/h}$  it was  $\Delta T=1.0$  K. Thus, the more is cooling rate, the more is supercooling of crystallization front. It happens because the more is cooling rate, the more is growth rate for one and the same period of time, after beginning of supercooling. The more is growth rate, the more interfacial supercooling should appear.

However as one can see in fig.2 and 3, the sample influence the measured value  $T_b$ . Thus, the value  $\Delta T$ , calculated by the expression (2) should be corrected. Such correction may be done if to represent the values of brightness temperature, obtained during melting and crystallization processes, as a dependence on the crystal length  $L$ . Fig.5 demonstrates these values, based on the data of fig.3, for cooling rate  $a = 40\text{K/h}$ . The value  $L$  was determined accordingly to the correlation  $L=L_0-h(t)$ , where  $L_0$  is the initial length of the sample.



**Fig. 5.** The dependence of the brightness temperature on sample length ( $L$ ) for heating and cooling process (cooling rate  $a = 40\text{K/h}$ ).

This method is based on the fact that the sample's own radiation at the optical properties and thermal conditions being constant, depends on its length. Therefore the reason of increasing of  $T_b^m(L)$  at decreasing of  $L$  from 32 to 30mm (fig.5) lies in the change of the

sample length influence on the value  $T_b$ . In this case determination of supercooling by the formula  $\Delta T = T_b^m(L) - T_b^c(L)$  excludes the influence of the sample on  $T_b$ . It is evident that the using of the latter expression lessens the value of supercooling by 0.5K for the studied sample at the time when its length was 32 mm.

#### 4. CONCLUSION

The study has shown that the high-resolution pyrometer ensured high long-term stability and high sensitivity of measurement of the interfacial temperature. The instrument was used to obtain the new experimental data for  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ . It is shown that the value  $\Delta T$ , obtained at the interfacial brightness temperature measurement for the growing crystal, may be overestimated. The experimental method to avoid this error is proposed.

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